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(71) Applicants: HENKEL CORPORATION [US/US]; Suite 200, 2500 Renaissance Boulevard, Gulph Mills, PA 19406 (US). HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN [DE/DE]; Henkelstrasse 67, D-40191 Dusseldorf (DE).

(72) Inventors: MILSTEIN, Norman; 9715 Zig Zag Road, Montgomery, OH 45242 (US). SALKA, Barry, A.; 3902 Knott Terrace, Fair Lawn, NJ 07410 (US). WADLE, Armin; 8, rue du Moulin à Vent, F-91590 Cerny (FR).

(74) Agent: TRZASKA, Steven, J.; Henkel Corporation, Suite 200, 2500 Renaissance Boulevard, Gulph Mills, PA 19406 (US).

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(54) Title: ALKYL POLYGLYCOSIDE ETHER CARBOXYLATES

#### (57) Abstract

A personal care product containing a surfactant corresponding to formula (I):  $R_1O(R_2O)_b(Z)_aOCH_2COO^-X^+$ , wherein  $R_1$  is a monovalent organic radical having from about 6 to about 30 carbon atoms;  $R_2$  is a divalent alkylene radical having from 2 to 4 carbon atoms; Z is a saccharide residue having 5 or 6 carbon atoms; Z is a number having a value from 1 to about 6; and Z is an alkali metal ion.

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#### ALKYL POLYGLYCOSIDE ETHER CARBOXYLATES

#### Field of the Invention

The present invention generally relates to alkyl polyglycoside ether carboxylates, their preparation, and to their use as surfactants.

## Background of the Invention:

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It is known that various surfactants have been found to be useful in cleaning compositions, such as shower gels, shampoos, and light-duty detergents such as dish washing detergents. In these types of compositions, good foamability is a prerequisite. The most widely used surfactants in these types of compositions are anionic surfactants such as alkyl sulfates, alkyl ether sulfates, sulfonates, sulfosuccinates and sarcosinates.

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Although the use of anionic surfactants in these compositions permits the attainment of desirable properties, including good foamability, the degree of foam stability leaves much to be desired. Foam stability relates to the ability of the foam, once formed, to remain intact for extended periods of time, thus enhancing the cleaning performance of the surfactant compositions.

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It is sometimes advantageous to use mixtures of surfactants in cleaning compositions when the surfactants can serve different functions, e.g., one serving to improve foamability and another serving to adjust viscosity. However, known surfactant mixtures typically provide a compromise between what can be achieved with the surfactant ingredients alone. For example, a mixture of more

costly surfactants such as amine oxides, betaines and alkanolamides which provide good foamability by themselves, with less expensive surfactants which provide poorer foamability will result in the formulation of a cleaning composition having an intermediate degree of foamability and poor foam stability.

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Alkyl polyglycosides are used as nonionic surfactants and are distinguished from other nonionic surfactants by their excellent detergent properties and high ecotoxicological compatibility. For this reason, this class of nonionic surfactants is acquiring increasing significance. They are generally used in liquid formulations, for example, dishwashing detergents and hair shampoos. However, because of their increased desirability as surface active agents, there use as surfactants in many other types of products is growing rapidly.

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While the use of mixtures of anionic and nonionic surfactants in most cases serves to further the objectives of both classes of surfactants, it would be much more desirable, and significantly less costly to employ, a single compound which would exhibit the favorable properties which are indigenous to both anionic and nonionic surfactants.

### Summary of the Invention:

The present invention provides a novel surfactant having general formula l:

$$R_1O(R_2O)_b(Z)_aOCH_2COO^-X^+$$

wherein R<sub>1</sub> is a monovalent organic radical having from about 6 to about 30

carbon atoms;  $R_2$  is a divalent alkylene radical having from 2 to 4 carbon atoms; Z is a saccharide residue having 5 or 6 carbon atoms; b is a number having a value from 0 to about 12; a is a number having a value from 1 to about 6; and X is an alkali metal ion.

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There is also provided a process for making novel surfactants involving:

(a) providing an alkyl polyglycoside having general formula II:

$$R_1O(R_2O)_b(Z)_a$$
 II

wherein  $R_1$  is a monovalent organic radical having from about 6 to about 30 carbon atoms;  $R_2$  is a divalent alkylene radical having from 2 to 4 carbon atoms; Z is a saccharide residue having 5 or 6 carbon atoms; b is a number having a value from 0 to about 12; a is a number having a value from 1 to about 6;

- (b) providing a non-aqueous alkali metal compound;
- (c) dispersing the alkyl polyglycoside in the nonaqueous alkali metal compound to form a reaction mixture; and

(d) adding an acetate derivative to the reaction mixture to form a reaction product.

#### **Description of the Invention:**

Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions are to be understood as being modified in all instances by the term "about".

The alkyl polyglycosides which can be used in the compositions according to the invention have the general formula II:

$$R_1O(R_2O)_b(Z)_a$$
 II

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wherein R<sub>1</sub> is a monovalent organic radical having from about 6 to about 30 carbon atoms; R<sub>2</sub> is a divalent alkylene radical having from 2 to 4 carbon atoms; Z is a saccharide residue having 5 or 6 carbon atoms; b is a number having a value from 0 to about 12; a is a number having a value from 1 to about 6. Preferred alkyl polyglycosides which can be used in the compositions according to the invention have the formula I wherein Z is a glucose residue and b is zero. Such alkyl polyglycosides are commercially available, for example, as APG®, GLUCOPON®, or PLANTAREN® surfactants from Henkel Corporation, Ambler, PA, 19002. Examples of such surfactants include but are not limited to:

- 1. APG® 225 Surfactant an alkyl polyglycoside in which the alkyl group contains 8 to 10 carbon atoms and has an average degree of polymerization of 1.7.
  - 2. GLUCOPON® 425 Surfactant an alkyl polyglycoside in which the alkyl group contains 8 to 16 carbon atoms and has an average degree of polymerization of 1.55.
    - 3. GLUCOPON® 625 Surfactant an alkyl polyglycoside in which the alkyl group contains 12 to 16 carbon atoms and have an average degree of polymerization of 1.6.
  - 4. APG® 325 Surfactant an alkyl polyglycoside in which the alkyl group contains 9 to 11 carbon atoms and have an average degree of polymerization of 1.6.
    - 5. GLUCOPON® 600 Surfactant an alkyl polyglycoside in which the alkyl group contains 12 to 16 carbon atoms and have an average degree of polymerization

of 1.4.

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- 6. PLANTAREN® 2000 Surfactant a  $C_{8-16}$  alkyl polyglycoside in which the alkyl group contains 8 to 16 carbon atoms and has an average degree of polymerization of 1.5.
- 7. PLANTAREN® 1300 Surfactant a  $C_{12-16}$  alkyl polyglycoside in which the alkyl group contains 12 to 16 carbon atoms and have an average degree of polymerization of 1.6.
  - 8. PLANTAREN® 1200 Surfactant a  $C_{12-16}$  alkylpolysaccharide in which the alkyl group contains 12 to 16 carbon atoms and have an average degree of polymerization of 1.4.

Other examples include alkyl polyglycoside surfactant compositions which are comprised of mixtures of compounds of formula I wherein Z represents a moiety derived from a reducing saccharide containing 5 or 6 carbon atoms; a is a number having a value from 1 to about 6; b is zero; and R<sub>1</sub> is an alkyl radical having from 8 to 20 carbon atoms. The compositions are characterized in that they have increased surfactant properties and an HLB in the range of about 10 to about 16 and a non-Flory distribution of glycosides, which is comprised of a mixture of an alkyl monoglycoside and a mixture of alkyl polyglycosides having varying degrees of polymerization of 2 and higher in progressively decreasing amounts, in which the amount by weight of polyglycoside having a degree of polymerization of 2, or mixtures thereof with the polyglycoside having a degree of polymerization of 3, predominate in relation to the amount of monoglycoside, said composition having an average degree of polymerization of about 1.8 to

about 3. Such compositions, also known as peaked alkyl polyglycosides, can be prepared by separation of the monoglycoside from the original reaction mixture of alkyl monoglycoside and alkyl polyglycosides after removal of the alcohol. This separation may be carried out by molecular distillation and normally results in the removal of about 70-95% by weight of the alkyl monoglycosides. After removal of the alkyl monoglycosides, the relative distribution of the various components, mono- and poly-glycosides, in the resulting product changes and the concentration in the product of the polyglycosides relative to the monoglycoside increases as well as the concentration of individual polyglycosides to the total, i.e., DP2 and DP3 fractions in relation to the sum of all DP fractions. Such compositions are disclosed in U.S. patent 5,266,690, the entire contents of which are incorporated herein by reference.

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Other alkyl polyglycosides which can be used in the compositions according to the invention are those in which the alkyl moiety contains from 6 to 18 carbon atoms in which and the average carbon chain length of the composition is from about 9 to about 14 comprising a mixture of two or more of at least binary components of alkylpolyglycosides, wherein each binary component is present in the mixture in relation to its average carbon chain length in an amount effective to provide the surfactant composition with the average carbon chain length of about 9 to about 14 and wherein at least one, or both binary components, comprise a Flory distribution of polyglycosides derived from an acid-catalyzed reaction of an alcohol containing 6-20 carbon atoms and a suitable saccharide from which excess alcohol has been separated.

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A particularly preferred alkyl polyglycoside of formula II is one wherein  $R_1$  is a monovalent organic radical having from 12 to 16 carbon atoms, b is zero, and a is a number having a value of about 1.4.

According to one aspect of the invention, there is provided a novel surfactant having general formula I:

$$R_1O(R_2O)_b(Z)_aOCH_2COO^-X^+$$

wherein  $R_1$  is a monovalent organic radical having from about 6 to about 30 carbon atoms;  $R_2$  is a divalent alkylene radical having from 2 to 4 carbon atoms; Z is a saccharide residue having 5 or 6 carbon atoms; b is a number having a value from 0 to about 12; a is a number having a value from 1 to about 6; and X is an alkali metal ion.

These novel surfactants possess both anionic and nonionic properties.

They provide superior levels of stable foam and act as viscosity builders when used in various types of detergent compositions.

In a particularly preferred embodiment of the novel surfactant of formula  $I, R_1$  is a monovalent organic radical having from 12 to 16 carbon atoms, b is zero, and a is a number having a value of about 1.4.

Another aspect of the present invention provides a process for making the above-disclosed novel surfactants. According to this aspect of the invention, the alkyl polyglycosides of formula II are etherified by reaction with a chloroacetate derivative such as, for example, sodium monochloroacetate. This reaction is carried out in a non-aqueous medium in the presence of alkali metal ions, preferably potassium or sodium ions. The alkali metal compound is preferably

employed in the form of an oxide such as, for example, sodium ethoxide, sodium hydroxide or potassium tert-butoxide.

In a preferred embodiment of the invention, about 1 mole of alkyl polyglycoside is first reacted with from about 1 to about 2 moles, and most preferably about 1 mole of alkali metal oxide to form a reaction mixture. This reaction is preferably carried out at a temperature ranging from about 70 to about 90°C, and most preferably about 80°C, and at a pH ranging from about 10 to about 14, and most preferably about 12.

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Once the reaction mixture is formed, from about 1 to about 2 moles, and preferably about 1 mole of a chloroacetate derivative is added to the reaction mixture. Examples of suitable chloroacetate derivatives include, but are not limited to, sodium monochloroacetate and ethyl chloroacetate. In a particularly preferred embodiment, the chloroacetate derivative is sodium monochloroacetate.

The chloroacetate derivative is added to the reaction mixture at a temperature ranging from about 60 to about 70°C, and a pH ranging from about 12 to about 14.

A procedure for making the novel surfactant is as follows. An alkyl polyglycoside is mixed with an organic reagent such as, for example, xylene or toluene, and subsequently heated in order to azeotropically remove any water contained in the alkyl polyglycoside, thus forming a mixture of anhydrous alkyl polyglycoside and solvent. This mixture is then heated to a temperature of about 70°C at which time an alkali metal compound is added. A solvent such as, for

example, ethanol may be added to the mixture in order to liquefy the mixture if needed. The chloroacetate derivative is then added to the reaction mixture, thereby etherifying the alkyl polyglycoside so as to form the novel surfactant of formula I.

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According to another aspect of the invention, there is provided a cleaning composition containing from about 20 to about 35% by weight, and preferably from about 25 to about 30% by weight of the novel surfactant of formula I, based on the weight of cleaning composition. The formulation of cleaning compositions may vary widely. It is well known that detergent and cleaning compositions contain surfactants and, in most cases, builders. While various surfactants, builders and additives may be employed in combination with the novel surfactant of formula I, the basis of this aspect of the invention is the presence of the surfactant of formula I in a cleaning composition, in the above-disclosed amounts.

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The following example is illustrative of the process and composition of the present invention and will be useful to one of ordinary skill in the art in practicing the invention. However, the invention is in no way limited by these examples.

### Example 1

A mixture of 650 grams (one mole) of a C<sub>12-16</sub> alkyl polyglycoside having an average degree of polymerization of 1.4 and 700 ml of toluene were heated in order to azeotropically distill any water present in the alkyl polyglycoside, using a Dean Stark trap. The temperature of the mixture rose from 85°C to 110°C. The distillation required about 4 hours. The dry alkyl polyglycoside was

clearly soluble in the toluene at room temperature. To this mixture, 485 grams (one mole) of ethanolic sodium hydroxide was added, with agitation. When the addition was complete, the reaction mixture was heated to about 60°C for about 1 hour, at which time 116.5 grams (one mole) of sodium monochloroacetate was added, with stirring, and was refluxed for about 5 hours. Water was then added in 200 ml increments while distilling, in 200 ml increments, the ternary azeotrope (toluene/ethanol/water) until the pot temperature reached about 100°C and only water remained in the product. This required about 8 hours. The distillate came off as two layers: the top layer being rich in toluene, and the bottom layer being rich in water. The top layer was used to azeotropically dry the next batch of alkyl polyglycoside starting material, the distillate initially consisting of the ternary azeotrope, toluene/ethanol/water, and finishing as the binary azeotrope, toluene/water. Wet analysis data performed on the residue is found in Table I below.

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Table I

Appearance at 25°C	Clear liquid	
Color, Gardner	4	
Solids, %	32.8	
pH (5% solids)	9.0	

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The alkyl polyglycoside ether carboxylates of the present invention may also be employed in personal care products such as cosmetic and pharmaceutical formulations. These personal care products include, for example, hair shampoos, hair lotions, bubble baths, skin creams, lotions, and ointments. Thus, according to another embodiment of the present invention,

there is provided a personal care composition containing an alkyl polyglycoside ether carboxylate in an amount of from about 0.1 to about 50% by weight, preferably from about 1 to about 25% by weight, and most preferably from about 2 to about 15% by weight, based on the weight of the personal care composition.

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Additional auxiliaries and additives which may also be employed in the personal care compositions of the present invention include, but are not limited to, mild surfactants, oily substances, emulsifiers, superfatting agents, pearly luster waxes, stabilizers, consistency-imparting agents, thickeners, cationic polymers, silicone compounds, biogenic active ingredients, anti-dandruff agents, film forming agents, preservatives, hydrotropes, solubilizers, UV light protection filters, insect repellents, artificial tanning agents, perfume oils, dyes, and the like.

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Typical examples of mild, i.e., particularly skin-compatible **surfactants** are fatty alcohol polyglycol ether sulfates, monoglyceride sulfates, mono- and/or dialkylsulfosuccinates, fatty acid isethionates, fatty acid sarcosinates, fatty acid taurides, fatty acid glutamates, ethercarboxylic acids, alkyl oligoglucosides, fatty acid glucamides, alkylamidobetaines, and/or protein-fatty acid condensates, the later preferably on the basis of wheat proteins.

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As **oily substances**, for example, Guerbet alcohols on the basis of fatty alcohols with 6 to 18, preferably 8 to 10 carbon atoms; esters of linear  $C_6$ - $C_{22}$  fatty acids with linear  $C_6$ - $C_{22}$  fatty alcohols; esters of branched  $C_6$ - $C_{13}$  carboxylic acids with linear  $C_6$ - $C_{22}$  fatty alcohols; esters of linear  $C_6$ - $C_{22}$  fatty acids with branched alcohols, especially 2-ethylhexanol; esters of linear and/or branched fatty acids with polyhydric alcohols (for example, ethylene glycol, dimer diol, or

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trimer triol) and/or Guerbet alcohols; triglycerides on the basis of  $C_8$ - $C_{10}$  fatty acids; esters of  $C_6$ - $C_{22}$  fatty alcohols and/or Guerbet alcohols with aromatic carboxylic acids, especially benzoic acid; esters of  $C_2$ - $C_{12}$  dicarboxylic acids with linear or branched alcohols with 1 to 22 carbon atoms or polyols with 2 to 10 carbon atoms and 2 to 6 hydroxyl groups; vegetable oils; branched primary alcohols; substituted cyclohexanes; linear  $C_6$ - $C_{22}$  fatty alcohol carbonates; Guerbet carbonates; esters of benzoic acid with linear and/or branched  $C_6$ - $C_{22}$  alcohols (e.g., FINSOLV® TN); dialkyl ethers; ring opening products of epoxidized fatty acid esters with polyols; silicone oils; and/or aliphatic or naphthenic hydrocarbons.

As emulsifiers, for example, nonionic surfactants from at least one of the following groups come under consideration:

- (1) Addition products of 2 to 30 moles ethylene oxide and/or 0 to 5 moles propylene oxide to linear fatty alcohols with 8 to 22 C atoms, to fatty acids with 12 to 22 C atoms and to alkylphenols with 8 to 15 C atoms in the alkyl group;
- (2)  $C_{12/18}$  fatty acid mono- and diesters of addition products of 1 to 30 moles ethylene oxide to glycerol;
- (3) glycerol mono- and diesters and sorbitan mono- and diesters of saturated and unsaturated fatty acids with 6 to 22 carbon atoms and their ethylene oxide addition products;
  - (4) alkyl mono- and oligoglycosides with 8 to 22 carbon atoms in the alkyl radical and their ethoxylated analogs;

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- (5) addition products of 15 to 60 moles ethylene oxide to castor oil and/or hardened castor oil;
- (6) polyol esters and especially polyglycerol esters, e.g., polyglycerol poly-12-hydroxystearate or polyglycerol dimerate. Also suitable are mixtures of compounds from several of these classes of substances;
- (7) addition products of 2 to 15 moles ethylene oxide to castor oil and/or hardened castor oil;
- (8) partial esters on the basis of linear, branched, unsaturated or saturated C<sub>6/22</sub> fatty acids, ricinoleic acid, and 12-hydroxystearic acid and glycerol, polyglycerol, pentaerythritol, dipentaerythritol, sugar alcohols (e.g., sorbitol), alkylglucosides (e.g., methylglucoside, butylglucoside, laurylglucoside) as well as polyglucosides (e.g., cellulose);
  - (9) mono-, di-, and trialkyl phosphates as well as mono-, di-, and/or tri-PEG-alkylphosphates;
- 15 (10) lanolin alcohols;
  - (11) polysiloxane-polyalkyl-polyether-copolymers or corresponding derivatives;
  - (12) mixed esters of pentaerythritol, fatty acids, citric acid, and fatty alcohol according to **German Patent (DE-PS) 1,165,574** and/or mixed esters of fatty acids with 6 to 22 carbon atoms, methylglucose, and polyols, preferably glycerol, as well as
  - (13) polyalkylene glycols.

The addition products of ethylene oxide and/or of propylene oxide to fatty alcohols, fatty acids, alkylphenols, glycerol mono- and diesters, as well as

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sorbitanmono- and diesters of fatty acids or to castor oil represent known, commercially available products. These are mixtures of homologs whose mean degree of alkoxylation corresponds to the ratio of ethylene oxide and/or propylene oxide and substrate with which the addition reaction is performed. C<sub>12/18</sub> fatty acid mono- and diesters of addition products of ethylene oxide to glycerol are known as refatting agents for cosmetic preparations from DE-PS 2,024,051.

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C<sub>8/18</sub> alkylmono- and -oligoglycosides, their preparation, and their use are known from the state of the art. Their manufacture is accomplished in particular by reacting glucose or oligosaccharides with primary alcohols with 8 to 18 C atoms. It is true of the glycoside radical that both monoglycosides, in the case of which a cyclic sugar radical is glucosidically bound to the fatty alcohol, and oligomeric glycosides with a degree of oligomerization up to preferably about 8 are suitable. The degree of oligomerization is a statistical mean value, based on a homolog distribution customary for such industrial products.

In addition, zwitterionic surfactants can be used as emulsifiers. Zwitterionic surfactants are defined as surface-active compounds that carry in the molecule at least one quaternary ammonium group and at least one carboxylate and one sulfonate group. Particularly suitable zwitterionic surfactants are the so-called betaines, such as N-alkyl-N,N-dimethylammonium glycinate, for example coco alkyldimethylammonium glycinate; N-acylamino-propyl-N,N-dimethylammonium glycinates, for example coco acylaminopropyldimethylammonium glycinate; and 2-alkyl-3-carboxymethyl-3-

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hydroxyethylimidazolines with in each case 8 to 18 C atoms in the alkyl or acyl group; as well as coco acylaminoethyl hydroxyethylcarboxymethyl glycinate. Particularly preferred is the fatty acid amide derivative known under the CTFA designation cocamidopropyl betaine. Also suitable as emulsifiers are ampholytic surfactants. Ampholytic surfactants are defined as surface-active compounds that, in addition to a  $C_{8/18}$  alkyl- or -acyl group in the molecule contain at least one free amino group and at least one -COOH- or SO<sub>3</sub>H group and are capable of forming internal salts. Examples of suitable ampholytic surfactants are N-N-alkylaminobutyric alkylglycines, N-alkylpropionic acids, acids, Nalkyliminodipropionic acids, N-hydroxyethyl-N-alkylamidopropylglycine, Nalkyltaurine, N-alkylsarcosine, 2-alkylaminopropionic acids and alkylaminoacetic acids with, in each case, 8 to 18 C atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-coco-alkylaminopropionate, coco acylamino-ethylamino-propionate, and C<sub>12/18</sub> acylsarcosine. In addition to the ampholytic emulsifiers, quaternary emulsifiers also come under consideration, wherein those of the type of the esterquats, preferably methylquaternized difatty acid triethanolamine ester salts, are particularly preferred.

As **superfatting agents**, substances such as lanolin and lecithin as well as polyethoxylated or acylated lanolin and lecithin derivatives, polyol fatty acid esters, monoglycerides, and fatty acid alkanolamides may be used, wherein the latter simultaneously serve as foam stabilizers.

As **pearl luster waxes**, the following come under consideration, for example: alkylene glycol esters, especially ethylene glycol distearate; fatty acid

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alkanolamides; especially coco fatty acid diethanolamide; partial glycerides, especially stearic acid monoglyceride; esters of polyfunctional, possibly hydroxy-substituted carboxylic acids with fatty alcohols with 6 to 22 carbon atoms, especially long-chain esters of tartaric acid; fats, for example fatty alcohols, fatty ketones, fatty aldehydes, fatty ethers and fatty carbonates, containing a total of at least 24 carbon atoms, especially laurone and distearyl ether; fatty acids such as stearic acid, hydroxystearic acid, or behenic acid; ring opening products of olefin epoxides with 12 to 22 carbon atoms with fatty alcohols with 12 to 22 carbon atoms and/or polyols with 2 to 15 carbon atoms and 2 to 10 hydroxyl groups; and mixtures thereof.

As consistency-imparting agents, fatty alcohols with 12 to 22 and preferably 16 to 18 carbon atoms as well as partial glycerides come under consideration. Preferred is a combination of these substances with alkyloligoglucosides and/or fatty acid-N-methylglucamides of the same chain length and/or polyglycerolpoly-12-hydroxystearates. Suitable thickeners are, for example, polysaccharides, especially xanthan gum, guar-guar, agar-agar, alginates and tyloses, carboxymethylcelluloses and hydroxyethylcelluloses, also high-molecular-weight polyethylene glycol mono- and diesters of fatty acids, polyacrylates (e.g., CARBOPOLS® from Goodrich or SYNTHALENS® from Sigma), polyacrylamides, polyvinyl alcohol and polyvinylpyrrolidone, surfactants such as ethoxylated fatty acid glycerides, esters of fatty acids with polyols such as pentaerythritol or trimethylolpropane, fatty alcohol ethoxylates, with narrow homolog distribution or alkyloligoglycosides as well as electrolytes such as

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sodium chloride and ammonium chloride.

Suitable cationic polymers are, for example, cationic cellulose derivatives, such as a quaternized hydroxyethylcellulose available from Amerchol under the name of POLYMER JR 400®; cationic starches; copolymers of diallylammonium salts and acrylamides; quaternized vinylpyrrolidone/ vinylimidazole polymers, such as LUVIQUAT® (BASF); condensation products of polyglycols and amines; quaternized collagen polypeptides, such as lauryldimonium hydroxypropyl hydrolyzed collagen (LAMEQUAT®/Gruenau); quaternized wheat polypeptides, polyethylene imine; cationic silicone polymers, e.g., amidomethicone; copolymers of adipic acid and dimethylaminohydroxypropyl diethylenetriamine (CARTARETINE®/ Sandoz); copolymers of adipic dimethyldiallylammonium chloride (MERQUAT® acid with 550/Chemviron); polyaminopolyamides, for example as described in FR-A 2,252,840 and crosslinked water-soluble polymers; cationic chitin derivatives such as quaternized chitosan, possibly with a microcrystalline distribution; condensation products of dihaloalkylene such as dibromobutane with bisdialkylamines, such as bis-dimethylamino-1,3-propane; cationic guar gums, such as JAGUAR® CBS, JAGUAR® C-17, GUAGUAR® C-16 from Celanese Corporation, quaternized ammonium salt polymers such as MIRAPOL® A-15, MIRAPOL® AD-1, MIRAPOL® AZ-1 from the Miranol company.

Suitable **silicone compounds** are, for example, dimethylpolysiloxanes, methylphenylpolysiloxanes, cyclic silicones, as well as amino, fatty acid, alcohol, polyether, epoxy, fluoro, glycoside, and/or alkyl-modified silicone compounds,

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which may exist in either liquid or resinous form at room temperature. Typical examples of fats are glycerides; as waxes, beeswax, carnauba wax, candelilla wax, montan wax, paraffin wax, or microwaxes, possibly in combination with hydrophilic waxes, e.g., cetylstearyl alcohol or partial glycerides, come under As stabilizers, metal salts of fatty acids, for example consideration. magnesium, aluminum, and/or zinc stearate may be used. As biogenic active ingredients, for example, tocopherol, tocopherol acetate, tocopherol palmitate, ascorbic acid, deoxyribonucleic acid, retinol, bisabolol, allantoin, phytanetriol, panthenol, AHA acids, amino acids, ceramides, pseudoceramides, essential oils, plant extracts, and vitamin complexes may be understood. As anti-dandruff agents, climbazole, octopirox, and zinc pyrithione may be used. Customary film-forming agents are, for example, chitosan, microcrystalline chitosan, quaternized chitosan, polyvinylpyrrolidone, vinylpyrrolidone-vinyl acetate copolymers, polymers of the acrylic acid series, quaternary cellulose derivatives, collagen, hyaluronic acids, and their salts and similar compounds. As swelling agents for aqueous phases, montmorillonites, clay minerals, pemulen and alkylmodified carbol types (Goodrich) may be used.

UV light protective filters are defined as organic substances that are capable of absorbing ultraviolet rays and releasing the energy taken up in the form of longer-wave radiation, for example heat. UVB filters can be oil-soluble or water-soluble. The following may be mentioned as examples of oil-soluble substances:

3-benzylidenecamphor and derivatives thereof, e.g., 3-(4-

- methylbenzylidene)camphor;
- 4-aminobenzoic acid derivatives, preferably 4-(dimethylamino) benzoic acid-2-ethylhexyl ester, 4-(dimethylamino) benzoic acid-2-octyl ester and 4-(dimethylamino) benzoic acid amyl ester;
- Esters of cinnamic acid, preferably 4-methoxycinnamic acid-2-ethylhexyl ester, 4-methoxycinnamic acid isopentyl ester, 2-cyano-3-phenylcinnamic acid-2-ethylhexyl ester (octocrylene);
  - Esters of salicylic acid, preferably salicylic acid-2-ethylhexyl ester,
     salicylic acid-4-isopropylbenzyl ester, salicylic acid homomenthyl ester;
- Derivatives of benzophenone, preferably 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxy-4'-methylbenzophenone,
   2,2'-dihydroxy-4-methoxybenzophenone;
  - Esters of benzalmalonic acid, preferably 4-methoxy-benzmalonic acid di-2-ethylhexyl ester;
- Triazine derivatives, such as 2,4,6-trianilino(p-carbo-2'-ethyl-1-hexyloxy)
  1,3,5-triazine and octyltriazone;
  - Propane-1,3-diones, such as 1-(4-tert.-butylphenyl)-3-(4-methoxyphenyl)propane-1,3-dione.

As water-soluble substances, the following may be considered:

- 2-Phenylbenzimidazole-5-sulfonic acids and the alkali, alkaline earth, ammonium, alkylammonium, alkanolammonium and glucammonium salts thereof;
  - Sulfonic acid derivatives of benzophenones, preferably 2-hydroxy-4-

methoxybenzophenone-5-sulfonic acids and salts thereof;

• Sulfonic acid derivatives of 3-benzylidenecamphor, for example, 4-(2-oxo-3-bornylidenemethyl)benzenesulfonic acid and 2-methyl-5-(2-oxo-3-bornylidene)sulfonic acid and salts thereof.

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Typical UV-A filters especially include derivatives of benzoylmethane, for example 1-(4'-tert-butylphenyl)-3-(4'-methoxyphenyl)propane-1,3-dione or 1phenyl-3-(4'-isopropylphenyl)-propane-1,3-dione. Naturally, the UV-A and UV-B filters can also be used in mixtures. In addition to the soluble substances mentioned, insoluble pigments, namely finely dispersed metal oxides or salts, come under consideration for this purpose, for example titanium dioxide, zinc oxide, iron oxide, aluminum oxide, cerium oxide, zirconium oxide, silicates (talc), barium sulfate, and zinc stearate. The particles should have a mean diameter of less than 100 nm, preferably between 5 and 50 nm and especially between 15 and 30 nm. They may have a spherical shape, but particles may also be used which have an ellipsoidal shape or a shape that differs from the spherical shape in some other way. In addition to the two above-mentioned groups of primary light-protective substances, secondary light-protective substances of the antioxidant type may be used, which intervene in the photochemical reaction chain initiated when UV radiation enters the skin. Typical examples are superoxide dismutase, tocopherols (vitamin E), and ascorbic acid (vitamin C). Additional suitable UV light-protective filters can be taken from the review by P. Finkel in **SÖFW-Journal** 122:5423, 1966.

In addition, to improve the flow behavior, hydrotropes, for example

ethanol, isopropyl alcohol, or polyols may be used. Polyols that come under consideration here preferably contain 2 to 15 carbon atoms and at least two hydroxyl groups. Typical examples are

Glycerol;

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- Alkylene glycols, such as ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, hexylene glycol, and polyethylene glycols with an average molecular weight of 100 to 1,000 daltons;
  - Technical oligoglycerol mixtures with an autocondensation degree of 1.5 to 10, for example technical diglycerol mixtures with a diglycerol content of 40 to 50 wt%;
    - Methylol compounds, especially trimethylolethane, trimethylolpropane, trimethylolbutane, pentaerythritol, and dipentaerythritol;
    - Lower alkyl glycosides, especially those with 1 to 8 carbon atoms in the alkyl radical, for example methyl- and butylglycoside;
- Sugar alcohols with 5 to 12 carbon atoms, for example sorbitol or mannitol;
  - Sugars with 5 to 12 carbon atoms, for example glucose or sucrose;
  - Amino sugars, for example glucamine.

Suitable **preservatives**, for example, include phenoxyethanol, formaldehyde solution, parabens, pentanediol, or sorbic acid. Suitable **insect repellents** include, for example, N,N-diethyl-m-toluamide, 1,2-pentanediol, or Insect Repellent 3535; a suitable **artificial tanning agent** is dihydroxyacetone.

Suitable perfume oils may include the extracts of flowers (lavender,

roses, jasmine, carnations), stems and leaves (geranium, patchouli, petitgrain), fruits (anise, coriander, caraway, juniper), fruit peelings (bergamot, lemon, orange), roots (mace, angelica, celery, cardamom, costus, iris, sweet flag), woods (sandalwood, guaiac wood, cedarwood, rosewood), herbs and grasses (tarragon, lemongrass, salvia, thyme), needles and branches (fir, spruce, pine, larch), resins and balsams (galbanum, elemi, benzoin, myrrh, olibanum, opoponax). Also, animal raw materials come under consideration, such as musk, civet, and castoreum. As synthetic or semisynthetic perfume oils, ambroxane, eugenol, isoeugenol, citronellal, hydroxycitronellal, geraniol, citronellol, geranyl acetate, citral, ionone, and methylionone come under consideration.

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As coloring materials, substances suitable and approved for cosmetic purposes can be used, as summarized for example in the publication "Cosmetic coloring materials" from the Dyestuffs Committee of the German Research Association, Verlag Chemie, Weinheim, 1984, pp. 81-106. These coloring materials are usually used in concentrations of 0.001 to 0.1 wt%, based on the total mixture.

The amount of auxiliaries and additives that may be employed can range from about 1 to about 50% by weight, and preferably from about 5 to about 40% by weight, based on the weight of the personal care composition. The production of the personal care composition may take place using any customary cold or hot processes; preferably the phase inversion temperature method.

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The present invention will be better understood from the examples which follow, all of which are intended to be illustrative only, and are not meant to unduly limit the scope of the invention in any way.

# **EXAMPLES**

	Hair rinse (I)			
	Hexadecyl Polyglucose (and) Hexadecyl Alcohol	4,0		
	Hydrolyzed Keratin	2,3		
5	Coco Glucosides	2,0		
	Sodium Coco Glucoside Carboxymethylate	1,0		
	Polyglyceryl-3-isostearat	1,0		
	Decyl Oleate	1,0		
	Glyceryl Stearate	0,5		
4.0				
10	Hair rinse (II)			
	Cetearyl Alcohol	2,5		
	Cationic wheat protein hydrolysate	1,0		
	Sodium Coco Glucoside Carboxymethylate	1,0		
45	Dicaprylyl Ether	1,0		
15	Ceteareth-20	0,8		
	Glyceryl Stearate	0,5		
	Hair rinse (III)			
	Cetearyl Alcohol	2,5		
	Cationic Wheat Protein Hydrolysate	1,0		
20	Sodium Coco Glucoside Carboxymethylate	0,5		
20	Octyldodecanol	1,0		
	Ceteareth-20	0,8		
	Glyceryl Stearate	0,5		
	Off-octive Octobrations	<u> </u>		
	Hair rinse (IV)			
25	Cetearyl Alcohol	2,5		
	Sodium Coco Glucoside Carboxymethylate	2,0		
	Cationic Wheat Protein Hydrolysate	1,0		
	Polyglyceryl-3 Diisostearat	1,0		
	Decyl Oleate	1,0		
30	Ceteareth-20	0,8		
	Glyceryl Stearate	0,5		
	Leave-on Hair Rinse			
	Polyacrylate (and) Laureth-2 (and) Paraffin Oil	3,0		
	Hydrolyzed Collagen	2,0		
35	Sodium Coco Glucoside Carboxymethylate	1,0		
	Cationic Wheat Protein Hydrolysate	8,0		
	Coco Glucosides	0,5		
	Oleyl Erucate	0,5		
	Tocopherol Acetate	0,2		
40	Ethanol	10,0		
	Glycerin (86 wt%)	5,0		

Hair treatment (I)	
Cetearyl Alcohol	
Sodium Coco Glucoside Carboxymethylate	
Cationic Wheat Protein Hydrolysate	
Ceteareth-20	
Glyceryl Stearate	
Hair treatment (II)	
Cetearyl Alcohol	
Cationic Wheat Protein Hydrolysate	
Ceteareth-20	
Sodium Coco Glucoside Carboxymethylate	
Octyldodecanol	
Glyceryl Stearate	
Shower liquid (I)	
Sodium Laureth Sulfate	
Coco Glucosides	
Sodium Coco Glucoside Carboxymethylate	
Laureth-2	
Cationic Wheat Protein Hydrolysate	
Shower liquid (II)	
Sodium Laureth Sulfate	
Coco Glucosides	
Glycol Distearate (and) Laureth-4 (and) Cocoamidopropyl Bet	aine
Laureth-2 (NRE)	
Glyceryl Laurate (and) Potassium Cocoyl Hydrolyzed Collage	n
Sodium Coco Glucoside Carboxymethylate	
NaCl	
Shower gel	
Sodium Laureth Sulfate	
Sodium Coco Glucoside Carboxymethylate	
Cocamidopropyl Betaine	
Coco Glucosides	
Glycol Distearate (and) Laureth-4 (and) Cocoamidopropyl Bet	aine
	n
Glyceryl Laurate (and) Potassium Cocoyl Hydrolyzed Collage	
Glyceryl Laurate (and) Potassium Cocoyl Hydrolyzed Collage Propylene Glycol (and) PEG-55 Propylene Glycol Oleate	
Propylene Glycol (and) PEG-55 Propylene Glycol Oleate	

	Washing lotion	
	Coco Glucosides (and) Sodium Laureth Sulfate	16,0
	Glycol Distearate (and) Laureth-4 (and) Cocamidopropyl Betaine	5,0
	Sodium Coco Glucoside Carboxymethylate	0,5
5	NaCl	1,5
	Shower liquid "Two-in-one" (I)	
	Sodium Laureth Sulfate	20,0
	Cocamidopropyl Betaine	20,0
	Coco Glucosides	5,0
10	Hydrolyzed Collagen	1,0
	Sodium Coco Glucoside Carboxymethylate	1,0
	Glycol Distearate (and) Laureth-4 (and) Cocamidopropyl Betaine	5,0
	Sodium Styrene/Acrylates Copolymer	2,0
	Laureth-2 (NRE)	0,6
15	Shower liquid "Two-in-one" (II)	
	Sodium Laureth Sulfate	20,0
	Cocamidopropyl Betaine	20,0
	Coco Glucosides	5,0
	Sodium Coco Glucoside Carboxymethylate	1,5
20	Glycol Distearate (and) Laureth-4 (and) Cocamidopropyl Betaine	3,0
	PEG-7 Glyceryl Cocoate	0,2
	Sodium Styrene/Acrylates Copolymer	1,0
	Laureth-2 (NRE)	0,6
	Glycerin (86 wt%)	5,0
0.5		
25	Shower liquid "Two-in-one" (III)	
	Sodium Laureth Sulfate	12,4
	Lauryl Glucosides	4,0
	Sodium Coco Glucoside Carboxymethylate	4,0
	Glycol Distearate (and) Laureth-4 (and) Cocamidopropyl Betaine	4,0
30	Panthenol	1,0
	Chaven limited and amoutains UTive in angle	
	Shower liquid and emulsion "Two-in-one"	27.0
	Coco Glucosides (and) sodium Laureth Sulfate	37,0
	Sodium Coco Glucoside Carboxymethylate	3,0
25	Ceteareth-20	1,0
35	Octyldodecanol	3,0
	Polyglyceryi-2-PEG-4 Copolymer	4,0
	Sodium Styrene/Acrylate Copolymer	1,0
	Cationic Wheat Protein Hydrolysate	1,0
	Perfume Oil	0,5

	Shampoo (I)				
	Sodium Laureth Sulfate	25,0			
	Coco Glucosides	5,0			
	Cocamidopropyl Betaine	8,0			
5	Sodium Coco Glucoside Carboxymethylate	3,0			
	Laureth-2 (NRE)	1,5			
	PPG-2-Ceteareth-9	1,0			
	Perfume Oil	5,0			
	Shampoo (II)				
10	Sodium Laureth Sulfate	11,0			
	Disodium Laureth Sulfosuccinate	7,0			
	Coco Glucosides	4,0			
	Sodium Coco Glucoside Carboxymethylate	1,0			
	Hydrolyzed Collagen	2,0			
15	NaCl	1,6			
	Shampoo (III)				
	Coco Glucosides (and) Sodium Laureth Sulfate	16,0			
	Sodium Coco Glucoside Carboxymethylate	2,0			
	NaCl	2,0			
20	Shampoo (IV)				
20	Coco Glucosides (and) Sodium Laureth Sulfate	17,0			
	Hydrolyzed Collagen	2,0			
	Sodium Coco Glucoside Carboxymethylate	2,0			
	Glycerin (86 wt%)	1,0			
25	Triethyleneglycol Distearate (and) Sodium Laureth Sulfate	3,0			
20	NaCl	2,2			
	1,40				
	Shampoo (V)				
	Sodium Laureth Sulfate	11,0			
	Coco Glucosides	6,0			
30	Hydrolyzed Collagen	2,0			
	Sodium Coco Glucoside Carboxymethylate	2,0			
	Triethyleneglycol Distearate (and) Sodium Laureth Sulfate	3,0			
	NaCl	3,0			
	Shampoo (VI)				
35	Ammonium Laureth Sulfate	23,0			
·	Coco Glucosides	4,0			
	Cocamidopropyl Betaine	7,0			
	Sodium Coco Glucoside Carboxymethylate	2,0			
	Hydrogenated Tallow Glycerides (and) Potassium Cocoyl Hydrolyzed Collagen	5,0			
40	Glyceryl Laurate	1,0			
	NaCl	3,0			

	Bubble bath (I)	22.0
	Coco Glucosides (and) Sodium Laureth Sulfate	22,0
	Cocamidopropyl Betaine Sodium Coco Glugosido Carboyumothylato	15,0
5	Sodium Coco Glucoside Carboxymethylate PEG-7 Glyceryl Cocoate	3,0
J	Glycol Distearate (and) Laureth-4 (and) Cocamidopropyl Betaine	2,0
	Glycol Distearate (and) Lauretti-4 (and) Cocarnidopropyr Detaine	5,0
	Bubble bath (II)	
	Sodium Laureth Sulfate	30,0
	Cocamidopropyl Betaine	10,0
10	Coco Glucosides	10,0
	Glyceryl Laurate (and) Potassium Cocoyl Hydrolyzed Collagen	4,0
	Sodium Coco Glucoside Carboxymethylate	2,0
	Hydrolyzed Wheat Protein	0,5
4 =	Bubble bath (III)	
15	Melissa oil	5,0
	PPG-7-Ceteareth-9	15,0
	Coco Glucosides	30,0
	Cocamidopropyl Betaine	10,0
	Sodium Coco Glucoside Carboxymethylate	4,0
20	Propylene Glycol (and) PEG-55 Propylene Glycol Oleate	3,8
	Laureth-2 (NRE)	1,5
	Bubble bath (IV)	
	Coco Glucosides (and) Sodium Laureth Sulfate	22,0
	Cocamidopropyl Betaine	15,0
25	Sodium Coco Glucoside Carboxymethylate	2,0
20	PEG-7 Glyceryl Cocoate	2,0
	Glycol Distearate (and) Laureth-4 (and) Cocamidopropyl Betaine	5,0
	Ciyoor Distearate (ana) Eaareti + (ana) Gocarniaopropyr Betaine	0,0
	Bubble bath concentrate	
	Sodium Laureth Sulfate	25,0
30	Coco Glucosides	20,0
	Cocamidopropyl Betaine	20,0
	Sodium Coco Glucoside Carboxymethylate	5,0
	PEG-7 Glyceryl Cocoate	5,0
	Hydrolyzed Collagen	2,0
35	PEG-60 Hydrogenated Caster Oil	5,0
	Citric acids (50 wt%)	0,5

	Night cream				
	Polyglyceryl-3 Diisostearate	4,0			
	Glyceryl Oleate	2,0			
	Beeswax	7,0			
5	Dicaprylyl Ether	5,0			
	Octyldodecanol	10,0			
	Coco Caprylate Caprate	5,0			
	Glycerin (86 wt%)	5,0			
	Magnesiumsulfat	1,0			
10	Sodium Coco Glucoside Carboxymethylate	5,0			
	Sunblock				
	Cetearylglucoside (and) Cetearyl Alcohol	4,0			
	Sodium Coco Glucoside Carboxymethylate	1,0			
	Hydrogenated Palm Glycerides	2,0			
15	Di-n-octylcarbonat	8,0			
	Coco Glycerides	6,0			
	Octyl Methoxycinnamate	5,0			
	4-Methylbenzyliden Camphor	3,0			
	Benzophenon-3	4,0			
20	Titanium dioxide	1,0			
	Zinc oxide	1,0			
	Octyl Triazone	1,0			
	Glycerin (86 wt%)	5,0			

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#### What is claimed is:

1. A personal care product comprising from about 0.1 to about 50% by weight of a surfactant corresponding to formula I:

$$R_1O(R_2O)_b(Z)_aOCH_2COO^-X^+$$

- wherein R<sub>1</sub> is a monovalent organic radical having from about 6 to about 30 carbon atoms; R<sub>2</sub> is a divalent alkylene radical having from 2 to 4 carbon atoms; Z is a saccharide residue having 5 or 6 carbon atoms; b is a number having a value from 0 to about 12; a is a number having a value from 1 to about 6; and X is an alkali metal ion.
- 10 2. The product of claim 1 wherein in formula I, R<sub>1</sub> is a monovalent organic radical having from 12 to 16 carbon atoms, b is zero, and a is a number having a value of about 1.4.
  - 3. The product of claim 1 wherein the surfactant is present in the product in an amount of from about 1 to about 25% by weight, based on the weight of the product.
  - 4. A process for making a novel surfactant comprising:
    - (a) providing an alkyl polyglycoside having general formula II:

$$R_1O(R_2O)_b(Z)_a$$

wherein  $R_1$  is a monovalent organic radical having from about 6 to about 30 carbon atoms;  $R_2$  is a divalent alkylene radical having from 2 to 4 carbon atoms; Z is a saccharide residue having 5 or 6 carbon atoms; b is a number having a value from 0 to about 12; a is a number having a value from 1 to about 6;

- (b) providing a non-aqueous alkali metal compound;
- (c) dispersing the alkyl polyglycoside in the nonaqueous alkali metal compound to form a reaction mixture; and
- (d) adding a chloroacetate derivative to the reaction mixture to form the novel surfactant.
- 5. The process of claim 4 wherein in formula II, R<sub>1</sub> is a monovalent organic

radical having from 12 to 16 carbon atoms, b is zero, and a is a number having a value of about 1.4.

- 6. The process of claim 4 wherein the alkali metal compound is selected from the group consisting of sodium ethoxide, sodium hydroxide, potassium tert-butoxide and mixtures thereof.
- 7. The process of claim 4 wherein the chloroacetate derivative is selected from the group consisting of sodium monochloroacetate, ethyl chloroacetate and mixtures thereof.
- 8. The process of claim 7 wherein the chloroacetate derivative is sodium monochloroacetate.
  - 9. The product of the process of claim 4.
  - 10. The product of the process of claim 5.
  - 11. The product of the process of claim 6.
  - 12. The product of the process of claim 7.
- 15 13. The product of the process of claim 8.
  - 14. A cleaning composition comprising from about 20 to about 35% by weight, based on the weight of the cleaning composition, of a surfactant having formula I:

$$R_1O(R_2O)_b(Z)_aOCH_2COO^-X^+$$

wherein  $R_1$  is a monovalent organic radical having from about 6 to about 30 carbon atoms;  $R_2$  is a divalent alkylene radical having from 2 to 4 carbon atoms; Z is a saccharide residue having 5 or 6 carbon atoms; b is a number having a value from 0 to about 12; a is a number having a value from 1 to about 6; and X is an alkali metal ion.

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/23230

A. CLASSIFICATION OF SUBJECT MATTER  IPC(6) :C11D 3/22; C07H 13/04, 15/08  US CL :510/470, 471; 536/4.1, 18.5, 120  According to International Patent Classification (IPC) or to both national classification and IPC  B. FIELDS SEARCHED				
	ocumentation searched (classification system followed	by classification symbols)		
	510/470, 471; 536/4.1, 18.5, 120	· · ·	-	
Documentat	ion searched other than minimum documentation to the	extent that such documents are included	in the fields searched	
	ata base consulted during the international search (nat	me of data base and, where practicable,	search terms used)	
C. DOC	UMENTS CONSIDERED TO BE RELEVANT			
Category*	Citation of document, with indication, where app	propriate, of the relevant passages	Relevant to claim No.	
A	US 4,599,188 A (LLENADO, R.) 08.	July 1986.	1-14	
A	US 4,806,275 A (JOHNSON ET AL.) 21 February 1989.		1-14	
A	US 5,179,201 A (OFTRING ET AL.)	12 January 1993.	1-14	
A	EP 0 070 076 A2 (THE PROCTER & GAMBLE COMPANY) 19 1-14 January 1983.			
A	EP 0 457 965 A1 (BALZER, D.) 27 November 1991.		1-14	
Furth	er documents are listed in the continuation of Box C.	See patent family annex.		
'A' do	ecial categories of cited documents:  cument defining the general state of the art which is not considered be of particular relevance	"T" later document published after the inte date and not in conflict with the app the principle or theory underlying the	lication but cited to understand e invention	
"E" earlier document published on or after the international filing date  "L" document which may throw doubts on priority claim(s) or which is		document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  document of particular relevance; the claimed invention cannot be		
special reason (as specified)  considered to the document referring to an oral disclosure use exhibition or other combined with the combin		considered to involve an inventive combined with one or more other such being obvious to a person skilled in	step when the document is h documents, such combination	
*P* document published prior to the international filing date but later than *&* document member of the same patent f the priority date claimed		t family		
Date of the actual completion of the international search  12 JANUARY 1999  Date of mailing of the international search report  0.2 FEB 1999				
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231  Facsimile No. (703) 305-3230  Authorized officer HOWARD C. LEE Anamente For				